H-atom parameters not refined

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.00$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1962, Vol. III)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg	0.25000	0.18949 (5)	0.00000	0.0417
Cl	0.2374 (1)	0.3981 (2)	0.2493 (2)	0.0476
C1	0.3757 (5)	0.1674 (8)	0.046 (1)	0.0443
N1	0.4435 (4)	0.155 (1)	0.0699 (9)	0.0588
N2	0.3824 (4)	0.3005 (8)	0.492 (1)	0.0571
C2	0.3828 (6)	0.143 (1)	0.501 (1)	0.0674
C3	0.4381 (6)	0.089 (1)	0.640 (1)	0.0629

Table 2. *Geometric parameters* (Å, °)

$\text{HgCl}_4(\text{CN})_2$ octahedron

Hg—Cl	2.901 (2)	Cl—Hg—Cl^i	92.64 (5)
Hg—Cl^i	3.432 (2)	Cl—Hg—Cl^{ii}	97.69 (6)
Hg—Cl	2.064 (9)	Cl—Hg—Cl^{iii}	167.65 (5)
Hg—N1	3.176 (7)	Cl^i—Hg—Cl^{iii}	77.99 (5)
		Cl—Hg—Cl	93.3 (2)
		Cl—Hg—Cl^i	78.5 (2)
		Cl—Hg—Cl^{iii}	92.7 (2)
		Cl—Hg—Cl^{ii}	94.1 (2)
		Cl—Hg—Cl^{ii}	168.8 (3)

Hg(CN)

Cl—N1	1.11 (1)	Hg—Cl—N1	179.6 (5)

$\text{C}_2\text{H}_5\text{NH}_3$

C2—N2	1.45 (1)	N2—C2—C3	111.5 (8)
C2—C3	1.52 (1)		

Hydrogen bridges

H1···N2	0.92 (1)	H2···Cl^{iv}	2.442 (2)
H1···Cl	2.233 (2)	H3···N2	0.92 (1)
H2···N2	0.92 (1)	H3···N1^v	2.078 (7)

Symmetry codes: (i) $2,[\tfrac{1}{4}y\tfrac{1}{4}]$; (ii) $2[\tfrac{1}{4}y0]$; (iii) $4[0\tfrac{1}{2}\tfrac{1}{2}]$; (iv) $2[\tfrac{1}{4}y\tfrac{1}{4}]$; (v) $\overline{1}[\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}]$.

The six standard reflections first showed a small increase then a small decrease in intensity indicating changing extinction behaviour. The positions of Hg and Cl atoms were determined by direct methods; a subsequent difference Fourier map revealed all N and C atoms. All H atoms could be found in correct positions on a difference Fourier map. Refinement, however, resulted in slightly deformed arrangements. Thus for the final refinement, H atoms were set at calculated positions and kept fixed. All computations were performed on a PC′386 with an adapted version of the program system *ATARI CRYSTAN*88 (Burzlaff & Rothammel, 1989).

References

Ahmed, F. R., Hall, S. H. & Huber, C. P. (1970). Editors. *Crystallographic Computing*, p. 292. Copenhagen: Munksgaard.

Ben Salah, A., Daoud, A., Bats, J. W. & Fuess, H. (1986). *J. Solid State Chem.* **65**, 151–155.

Ben Salah, A., Daoud, A., Constant, G., Jaud, J. & Galy, J. (1983). *Acta Cryst.* C39, 63–66.

Birgeneau, R. J., Shirane, G. & Kitchens, T. A. (1974). *J. Low Temp. Phys.* **14**, 373–385.

Burzlaff, H. & Rothammel, W. (1989). *Proceedings of the CIC Meeting, Tübingen*, pp. 415–421. Berlin: Springer-Verlag.

Dupas, C. & Renard, J. P. (1973). *Phys. Lett. A*, **43**, 119–120.

Grdenic, D. (1965). *Q. Rev. Chem. Soc.* **19**, 303–328.

Hoppe, R., Wilhelm, V. & Müller, B. (1972). *Z. Anorg. Allg. Chem.* **392**, 1–9.

Mashiyama, A. (1980). *J. Phys. Soc. Jpn*, **49**, 2270–2277.

Sandström, M. (1978). Thesis, Univ. of Stockholm, Sweden.

Subramanian, V. & Seff, K. (1980). *Acta Cryst.* B36, 2132–2135.

A Monodentate 1,3-Diphenyl-2-triazeno Terpyridineplatinum(II) Complex

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Abstract

The compound (1,3-diphenyl-2-triazeno)(2,2′,2″-terpyridine)platinum(II) perchlorate dimethylformamide solvate (1) is formed by reaction of dpt (dptH = 1,3-diphenyltriazene) and [Pt(tpy)Cl]Cl (tpy = terpyridine) in the presence of excess base (NEt₃). There are two independent cations in the asymmetric unit. The platinum centers have a monodentate triazeno ligand with the remaining coordination sites occupied by the terpyridine group. The crystal packing is dominated by π–π stacking interactions, and metal–metal interactions are conspicuously absent.

Comment

Both metal–metal (Smith, Miskowski, Mason & Gray, 1990; Rice, Miskowski & Gray, 1987; Stiegman, Rice, Gray & Miskowski, 1987; Rice & Gray, 1983) and ligand(π)–ligand(π) (Miskowski &

† Contribution No. 8734.

Houlding, 1991) interactions can strongly influence the spectroscopic properties of (α-diimine)platinum complexes. Our recent work in this area has centered on the triazenido ligand because it is well known to form bridged complexes with relatively short metal–metal distances (Moore & Robinson, 1986). Mononuclear monodentate triazenido complexes are relatively rare, and the limited examples occur mostly with the platinum-group metals (Bombieri, Immirzi & Toniolo, 1976; Brown & Ibers, 1976a,b). We have prepared a mononuclear complex [Pt(tpy)-(dpt)](ClO₄) (1) (dptH = 1,3-diphenyltriazene, tpy = terpyridine) with a monodentate dpt ligand; this complex is deep green and displays dichroic behavior. The crystal and molecular structure of (1) is described herein.

Fig. 1. A drawing of the cations (50% probability ellipsoids for anisotropic atoms) showing the numbering system. H atoms are not shown.

Cation of (1)

Compound (1) was prepared by reaction of [Pt(tpy)Cl]Cl.H₂O in aqueous acetone with one half equivalent of dpt and excess Et₃N. Although the stoichiometry should have promoted binuclear complex formation, the triazeno-bridged species was not detected. Small deep-red tabular blocks were grown by slow diffusion of ether into a DMF (dimethylformamide) solution. There are two independent cations in the structure, which are shown in Fig. 1 with atom labels; Fig. 2 shows the packing arrangement aligned to show the aromatic ring stacking. The restricted bite angle of the tridentate terpyridine ligand has caused a small distortion at each Pt atom from a square-planar geometry; this distortion is commonly observed in terpyridine complexes (Dewan, Lippard & Bauer, 1980; Ratilla, Scott, Moxness & Kostic, 1990; Wong & Lippard, 1977; Jennette, Gill, Sadownick & Lippard, 1976; Bailey & Gray, 1992; Bailey, Miskowski & Gray, 1993). As a consequence, the cis N—Pt—N angles within the four metallocyclic rings are less than 90° (between 80.1 and 80.7°). The Pt(1)—N(2) and the Pt(2)—N(8) lengths are relatively short [1.941 (10) and 1.943 (9) Å]; this also is a result of the geometrical constraints imposed by the tpy ligand.

The remaining bond lengths and angles in the cations are unremarkable; however, extensive inter-

Fig. 2. A drawing showing stacking interactions between cations. Pt and N atoms are shown as 50% probability ellipsoids; C atoms as 10%; H atoms are not shown.

molecular interactions between cations occur via stacking of the π systems of both the terpyridine and triazeno ligands. The interaction involves aromatic rings from four neighboring molecules (see Fig. 2); two tpy ligands [one from a Pt(1) and one from a Pt(2) fragment] form the interior of a short stack and have a closest contact of under 3.4 Å [C(12)···N(8) 3.387 (16), C(14)···N(7) 3.316 (15) Å]. This distance is well within the value (3.8 Å) normally associated with a significant π–π interaction (Hunter & Sanders, 1990). The stack is completed on each side by a phenyl group from a triazeno ligand. The Pt(1) side is capped by an α-phenyl group with closest contacts of just over 3.4 Å [C(46)···N(3) 3.489 (15), C(47)···C(11) 3.454 (18) Å], while the Pt(2) side has a γ-phenyl at around 3.4 Å [C(52)···C(34) 3.348 (19), C(49)···C(31) 3.416 (18) Å]. These two phenyl groups are both from Pt(2) fragments. Each set of four aromatic systems is linked to the

next through a Pt(2) fragment to form a helical network throughout the crystal. Although Pt^{II} compounds are known to aggregate into oligomeric chains supported by metal–metal interactions only, the platinum–platinum distances far exceed those that are close enough for appreciable bonding. The closest approach is between Pt(1) and Pt(2) [6.913 (6) Å], and all other Pt···Pt distances are greater than 8 Å. The stacking in this crystal structure exclusively involves the aromatic π systems.

Experimental

Crystal data

{[Pt(C$_{15}$H$_{11}$N$_3$)(C$_{12}$H$_{10}$N$_3$)]-(ClO$_4$).C$_3$H$_7$NO}$_2$
$M_r = 1594.30$
Monoclinic
$P2_1/c$
$a = 15.610$ (4) Å
$b = 14.809$ (5) Å
$c = 25.918$ (9) Å
$\beta = 92.34$ (2)°
$V = 5986$ (3) Å^3
$Z = 4$

$D_x = 1.77$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 6.35–12.42°$
$\mu = 4.830$ mm^{-1}
$T = 130$ K
Rods
Red-brown
Crystal source: DMF/ether

Data collection

Nicolet $R3m/V$ diffractometer
ω scans
Absorption correction: refined from ΔF
$T_{min} = 0.806$, $T_{max} = 0.833$
10552 measured reflections
10552 independent reflections

6961 observed reflections $[F>4\sigma(F)]$
$\theta_{max} = 25°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 30$
2 standard reflections monitored every 198 reflections intensity variation: ±2%

Refinement

Refinement on F
Final $R = 0.056$
$wR = 0.058$
$S = 1.09$
6961 reflections
476 parameters
$w = 1/[\sigma^2(F)+0.0004F^2]$

$(\Delta/\sigma)_{max} = 0.11$ for C(33); 0.02 for all others
$\Delta\rho_{max} = 1.63$ e Å^{-3}
$\Delta\rho_{min} = -1.19$ e Å^{-3}
Atomic scattering factors from Cromer (1974); Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt(1)	0.1212 (1)	0.0487 (1)	0.1994 (1)	0.0023 (1)
Pt(2)	-0.4375 (1)	0.0821 (1)	0.1947 (1)	0.0022 (1)
Cl(1)	0.1322 (2)	0.1770 (2)	0.0275 (1)	0.0034 (1)
Cl(2)	0.6442 (2)	0.1817 (2)	0.0405 (1)	0.0035 (1)
O(1)	0.0472 (7)	0.1915 (8)	0.0079 (5)	0.0079 (5)
O(2)	0.1889 (8)	0.2368 (7)	0.0032 (4)	0.0073 (5)
O(3)	0.1389 (7)	0.1921 (8)	0.0823 (3)	0.0068 (5)
O(4)	0.1556 (7)	0.0860 (6)	0.0173 (4)	0.0061 (4)
O(5)	0.6483 (8)	0.1881 (10)	0.0943 (4)	0.0096 (6)
O(6)	0.6886 (10)	0.2517 (10)	0.0187 (6)	0.0117 (7)
O(7)	0.5567 (7)	0.1778 (9)	0.0212 (4)	0.0091 (6)
O(8)	0.6842 (7)	0.0974 (8)	0.0267 (5)	0.0082 (5)
N(1)	0.0127 (6)	0.0657 (7)	0.1549 (4)	0.0028 (4)
N(2)	0.1451 (6)	-0.0344 (7)	0.1439 (4)	0.0025 (3)
N(3)	0.2393 (6)	0.0057 (7)	0.2235 (3)	0.0025 (3)
N(4)	0.0967 (6)	0.1367 (7)	0.2582 (3)	0.0025 (3)
N(5)	0.0723 (6)	0.1053 (7)	0.3036 (4)	0.0030 (4)
N(6)	0.0758 (7)	0.0195 (8)	0.3080 (4)	0.0035 (4)
N(7)	-0.5249 (6)	0.1686 (7)	0.2221 (3)	0.0026 (3)
N(8)	-0.5261 (7)	0.0700 (6)	0.1403 (3)	0.0026 (3)
N(9)	-0.3795 (6)	-0.0090 (7)	0.1489 (3)	0.0026 (3)
N(10)	-0.3450 (6)	0.0949 (6)	0.2515 (4)	0.0024 (3)
N(11)	-0.3401 (6)	0.0421 (7)	0.2932 (3)	0.0019 (3)
N(12)	-0.4015 (6)	-0.0153 (7)	0.2968 (4)	0.0028 (3)
C(1)	-0.0544 (8)	0.1191 (9)	0.1640 (5)	0.0030 (3)
C(2)	-0.1252 (8)	0.1257 (9)	0.1303 (5)	0.0034 (3)
C(3)	-0.1274 (9)	0.0709 (9)	0.0865 (5)	0.0039 (4)
C(4)	-0.0602 (8)	0.0163 (9)	0.0774 (5)	0.0036 (3)
C(5)	0.0086 (8)	0.0106 (9)	0.1111 (4)	0.0026 (3)
C(6)	0.0856 (8)	-0.0450 (9)	0.1050 (4)	0.0025 (3)
C(7)	0.1003 (8)	-0.1071 (9)	0.0668 (5)	0.0032 (3)
C(8)	0.1760 (9)	-0.1519 (10)	0.0679 (5)	0.0042 (4)
C(9)	0.2386 (8)	-0.1382 (9)	0.1068 (5)	0.0031 (3)
C(10)	0.2215 (8)	-0.0792 (9)	0.1456 (4)	0.0026 (3)
C(11)	0.2748 (8)	-0.0549 (8)	0.1913 (4)	0.0026 (3)
C(12)	0.3572 (8)	-0.0876 (9)	0.2010 (4)	0.0027 (3)
C(13)	0.4050 (8)	-0.0562 (8)	0.2441 (5)	0.0031 (3)
C(14)	0.3668 (8)	0.0048 (8)	0.2775 (4)	0.0026 (3)
C(15)	0.2849 (8)	0.0354 (8)	0.2661 (4)	0.0026 (3)
C(16)	0.1016 (8)	0.2299 (8)	0.2537 (4)	0.0025 (3)
C(17)	0.0931 (8)	0.2875 (8)	0.2962 (5)	0.0029 (3)
C(18)	0.0967 (9)	0.3806 (10)	0.2895 (5)	0.0040 (4)
C(19)	0.1088 (9)	0.4202 (10)	0.2406 (5)	0.0044 (4)
C(20)	0.1158 (9)	0.3605 (9)	0.1992 (5)	0.0041 (4)
C(21)	0.1128 (8)	0.2688 (9)	0.2056 (5)	0.0033 (3)
C(22)	0.0438 (9)	-0.0098 (9)	0.3552 (5)	0.0035 (3)
C(23)	0.0617 (8)	-0.1009 (9)	0.3700 (5)	0.0035 (3)
C(24)	0.0266 (9)	-0.1342 (10)	0.4140 (5)	0.0042 (4)
C(25)	-0.0280 (10)	-0.0856 (11)	0.4428 (6)	0.0052 (4)
C(26)	-0.0465 (11)	0.0021 (12)	0.4284 (6)	0.0061 (5)
C(27)	-0.0132 (9)	0.0399 (10)	0.3849 (5)	0.0041 (4)
C(28)	-0.5208 (9)	0.2144 (9)	0.2663 (5)	0.0035 (3)
C(29)	-0.5864 (8)	0.2669 (9)	0.2814 (5)	0.0034 (3)
C(30)	-0.6617 (9)	0.2741 (9)	0.2512 (5)	0.0035 (3)
C(31)	-0.6661 (8)	0.2247 (9)	0.2052 (5)	0.0034 (3)
C(32)	-0.5974 (7)	0.1742 (8)	0.1904 (4)	0.0021 (3)
C(33)	-0.5984 (8)	0.1196 (8)	0.1448 (4)	0.0027 (3)
C(34)	-0.6639 (8)	0.1084 (9)	0.1064 (5)	0.0031 (3)
C(35)	-0.6516 (9)	0.0474 (9)	0.0669 (5)	0.0038 (3)
C(36)	-0.5785 (8)	-0.0008 (9)	0.0640 (5)	0.0031 (3)
C(37)	-0.5134 (8)	0.0102 (8)	0.1023 (4)	0.0026 (3)
C(38)	-0.4298 (8)	-0.0341 (9)	0.1075 (5)	0.0031 (3)
C(39)	-0.3999 (8)	-0.0939 (9)	0.0718 (5)	0.0035 (3)
C(40)	-0.3195 (9)	-0.1297 (9)	0.0781 (5)	0.0038 (3)
C(41)	-0.2687 (9)	-0.1072 (9)	0.1202 (5)	0.0039 (4)
C(42)	-0.3007 (8)	-0.0447 (8)	0.1550 (5)	0.0029 (3)
C(43)	-0.2792 (7)	0.1604 (8)	0.2508 (4)	0.0023 (3)
C(44)	-0.2075 (8)	0.1588 (9)	0.2863 (5)	0.0030 (3)
C(45)	-0.1450 (8)	0.2261 (9)	0.2838 (5)	0.0034 (3)
C(46)	-0.1511 (8)	0.2957 (9)	0.2486 (5)	0.0034 (3)
C(47)	-0.2222 (8)	0.2946 (9)	0.2132 (5)	0.0036 (3)
C(48)	-0.2862 (8)	0.2302 (8)	0.2147 (5)	0.0030 (3)
C(49)	-0.3901 (8)	-0.0689 (8)	0.3415 (4)	0.0027 (3)
C(50)	-0.4618 (9)	-0.1125 (9)	0.3593 (5)	0.0037 (3)
C(51)	-0.4582 (10)	-0.1667 (10)	0.4020 (5)	0.0047 (4)
C(52)	-0.3800 (9)	-0.1789 (10)	0.4275 (5)	0.0045 (4)
C(53)	-0.3075 (9)	-0.1388 (10)	0.4112 (5)	0.0037 (3)
C(54)	-0.3115 (8)	-0.0831 (9)	0.3671 (5)	0.0032 (3)
N(13)	0.2612 (9)	0.0416 (10)	0.4298 (5)	0.0064 (4)
O(9)	0.3242 (8)	0.1357 (9)	0.3744 (5)	0.0080 (4)
C(55)	0.2005 (12)	0.0299 (13)	0.4681 (7)	0.0090 (6)
C(56)	0.3022 (12)	-0.0407 (13)	0.4130 (7)	0.0090 (7)
C(57)	0.2701 (12)	0.1216 (13)	0.4082 (7)	0.0071 (5)
N(14)	0.4297 (8)	0.6469 (8)	0.0769 (4)	0.0044 (3)
O(10)	0.4410 (6)	0.7781 (7)	0.1227 (4)	0.0051 (3)
C(58)	0.3393 (9)	0.6373 (11)	0.0852 (6)	0.0056 (4)
C(59)	0.4659 (11)	0.5827 (11)	0.0421 (6)	0.0072 (5)
C(60)	0.4707 (11)	0.7162 (11)	0.0952 (6)	0.0060 (5)

Table 2. *Geometric parameters* (Å, °)

Pt(1)—N(1)	2.025 (10)	C(1)—C(2)	1.383 (17)
Pt(1)—N(2)	1.941 (10)	C(2)—C(3)	1.395 (18)
Pt(1)—N(3)	2.025 (10)	C(3)—C(4)	1.354 (19)
Pt(1)—N(4)	2.052 (10)	C(4)—C(5)	1.359 (17)
Pt(2)—N(7)	2.021 (10)	C(5)—C(6)	1.472 (17)
Pt(2)—N(8)	1.943 (9)	C(6)—C(7)	1.377 (17)
Pt(2)—N(9)	2.034 (10)	C(7)—C(8)	1.356 (19)
Pt(2)—N(10)	2.026 (9)	C(8)—C(9)	1.390 (18)
N(1)—C(1)	1.341 (16)	C(9)—C(10)	1.366 (17)
N(1)—C(5)	1.398 (15)	C(10)—C(11)	1.466 (16)
N(2)—C(6)	1.352 (15)	C(11)—C(12)	1.388 (17)
N(2)—C(10)	1.363 (15)	C(12)—C(13)	1.397 (16)
N(3)—C(11)	1.359 (15)	C(13)—C(14)	1.401 (17)
N(3)—C(15)	1.363 (15)	C(14)—C(15)	1.377 (17)
N(4)—N(5)	1.334 (14)	C(28)—C(29)	1.355 (19)
N(4)—C(16)	1.388 (16)	C(29)—C(30)	1.390 (18)
N(5)—N(6)	1.278 (16)	C(30)—C(31)	1.396 (18)
N(6)—C(22)	1.407 (17)	C(31)—C(32)	1.375 (17)
N(7)—C(28)	1.332 (15)	C(32)—C(33)	1.432 (16)
N(7)—C(32)	1.373 (14)	C(33)—C(34)	1.407 (17)
N(8)—C(33)	1.355 (16)	C(34)—C(35)	1.384 (18)
N(8)—C(37)	1.346 (15)	C(35)—C(36)	1.351 (19)
N(9)—C(38)	1.354 (15)	C(36)—C(37)	1.400 (17)
N(9)—C(42)	1.343 (15)	C(37)—C(38)	1.462 (17)
N(10)—N(11)	1.335 (13)	C(38)—C(39)	1.376 (18)
N(10)—C(43)	1.414 (15)	C(39)—C(40)	1.366 (19)
N(11)—N(12)	1.287 (14)	C(40)—C(41)	1.364 (18)
N(12)—C(49)	1.409 (15)	C(41)—C(42)	1.397 (18)
N(1)—Pt(1)—N(2)	80.7 (4)	Pt(2)—N(10)—C(43)	123.5 (7)
N(1)—Pt(1)—N(3)	160.8 (4)	N(11)—N(10)—C(43)	113.2 (9)
N(2)—Pt(1)—N(3)	80.1 (4)	N(1)—C(1)—C(2)	122.8 (11)
N(1)—Pt(1)—N(4)	99.6 (4)	C(1)—C(2)—C(3)	117.7 (12)
N(2)—Pt(1)—N(4)	179.6 (5)	C(2)—C(3)—C(4)	119.7 (12)
N(3)—Pt(1)—N(4)	99.5 (4)	C(3)—C(4)—C(5)	121.5 (12)
N(7)—Pt(2)—N(8)	80.9 (4)	N(1)—C(5)—C(4)	119.7 (11)
N(7)—Pt(2)—N(9)	161.4 (4)	N(1)—C(5)—C(6)	113.7 (10)
N(8)—Pt(2)—N(9)	80.5 (4)	C(12)—C(13)—C(14)	118.8 (11)
N(7)—Pt(2)—N(10)	99.0 (4)	C(13)—C(14)—C(15)	119.7 (11)
N(8)—Pt(2)—N(10)	180.0 (5)	N(3)—C(15)—C(14)	121.1 (11)
N(9)—Pt(2)—N(10)	99.6 (4)	N(4)—C(16)—C(17)	122.0 (10)
Pt(1)—N(1)—C(1)	128.0 (8)	N(4)—C(16)—C(21)	119.8 (11)
Pt(1)—N(1)—C(5)	113.6 (8)	C(17)—C(16)—C(21)	118.2 (11)
C(1)—N(1)—C(5)	118.4 (10)	N(6)—C(22)—C(23)	116.9 (12)
Pt(1)—N(2)—C(6)	118.6 (8)	N(6)—C(22)—C(27)	124.7 (12)
Pt(1)—N(2)—C(10)	118.7 (7)	N(7)—C(28)—C(29)	122.0 (12)
C(6)—N(2)—C(10)	122.7 (10)	N(7)—C(32)—C(31)	120.0 (10)
Pt(1)—N(3)—C(11)	114.1 (7)	N(7)—C(32)—C(33)	116.1 (10)
Pt(1)—N(3)—C(15)	125.9 (8)	C(31)—C(32)—C(33)	123.7 (10)
C(11)—N(3)—C(15)	119.9 (10)	N(8)—C(33)—C(32)	113.3 (10)
Pt(1)—N(4)—N(5)	120.1 (8)	N(8)—C(33)—C(34)	117.3 (11)
Pt(1)—N(4)—C(16)	123.8 (7)	N(8)—C(37)—C(36)	118.1 (11)
N(5)—N(4)—C(16)	116.1 (10)	N(8)—C(37)—C(38)	112.7 (10)
N(4)—N(5)—N(6)	114.4 (10)	C(36)—C(37)—C(38)	129.2 (11)
N(5)—N(6)—C(22)	111.7 (10)	N(9)—C(38)—C(37)	115.8 (11)
Pt(2)—N(7)—C(28)	128.0 (8)	N(9)—C(38)—C(39)	120.5 (11)
Pt(2)—N(7)—C(32)	112.4 (7)	C(37)—C(38)—C(39)	123.6 (11)
C(28)—N(7)—C(32)	119.5 (10)	C(38)—C(39)—C(40)	120.4 (12)
Pt(2)—N(8)—C(33)	117.3 (7)	C(39)—C(40)—C(41)	120.1 (13)
Pt(2)—N(8)—C(37)	118.0 (8)	C(44)—C(43)—C(48)	119.0 (11)
C(33)—N(8)—C(37)	124.6 (10)	C(43)—C(44)—C(45)	119.5 (11)
Pt(2)—N(9)—C(38)	112.8 (8)	C(44)—C(45)—C(46)	122.2 (12)
Pt(2)—N(9)—C(42)	128.3 (8)	C(45)—C(46)—C(47)	117.0 (12)
C(38)—N(9)—C(42)	118.9 (10)	N(12)—C(49)—C(50)	117.3 (11)
Pt(2)—N(10)—N(11)	123.3 (7)	N(12)—C(49)—C(54)	123.9 (11)

The data were collected using a Nicolet *R*3*m*/*V* diffractometer equipped with a locally modified Enraf–Nonius low-temperature apparatus. One unique data set was collected and used in the refinement. The data were corrected for absorption using *XABS* (H. Hope & B. Moezzi, Chemistry Department, University of California, Davis, California, USA) a program which provides an empirical correction based on F_o and F_c differences. Calculations were performed with *SHELXTL*

(Sheldrick, 1984) installed on a MicroVAX computer. The Pt-atom coordinates were determined from the Patterson map and remaining atoms were located with subsequent cycles of least-squares refinement and calculation of difference Fourier maps. The H-atom positions were calculated using a riding model with a C—H vector fixed at 0.96 Å and a thermal parameter of 0.04 Å^2. All non-C atoms excluding those of the solvent of crystallization were refined with anisotropic thermal parameters, while all other atoms were refined with isotropic thermal parameters.

The asymmetric unit contains two crystallographically independent cations, two perchlorate anions and two molecules of *N*,*N*-dimethylformamide. The cations are in close π contact with each other.

References

Bailey, J. A. & Gray, H. B. (1992). *Acta Cryst.* C48, 1420–1422.
Bailey, J. A., Miskowski, V. M. & Gray, H. B. (1993). *Acta Cryst.* C49, 793–796.
Bombieri, G., Immirzi, A. & Toniolo, L. (1976). *Inorg. Chem.* 15, 2428–2432.
Brown, L. D. & Ibers, J. A. (1976*a*). *J. Am. Chem. Soc.* 98, 1597–1598.
Brown, L. D. & Ibers, J. A. (1976*b*). *Inorg. Chem.* 15, 2794–2798.
Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Dewan, J. C., Lippard, S. J. & Bauer, W. R. (1980). *J. Am. Chem. Soc.* 102, 858–860.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* 112, 5525–5534.
Jennette, K. W., Gill, J. T., Sadownick, J. A. & Lippard, S. J. (1976). *J. Am. Chem. Soc.* 98, 6159–6168.
Miskowski, V. M. & Houlding, V. H. (1991). *Inorg. Chem.* 30, 4446–4452.
Moore, D. S. & Robinson, S. D. (1986). *Adv. Inorg. Chem. Rad.* 30, 1–68, and references therein.
Ratilla, E. M. A., Scott, B. K., Moxness, M. S. & Kostic, N. M. (1990). *Inorg. Chem.* 29, 918–926.
Rice, S. F. & Gray, H. B. (1983). *J. Am. Chem. Soc.* 105, 4571–4575.
Rice, S. F., Miskowski, V. M. & Gray, H. B. (1987). *Inorg. Chem.* 27, 4704–4708.
Sheldrick, G. M. (1984). *SHELXTL User's Manual.* Revision 4.11. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Smith, D. C., Miskowski, V. M., Mason, W. R. & Gray, H. B.
  (1990). *J. Am. Chem. Soc.* **112**, 3752–3767.
Stiegman, A. E., Rice, S. F., Gray, H. B. & Miskowski, V. M.
  (1987). *Inorg. Chem.* **26**, 1112–1116.
Wong, Y.-S. & Lippard, S. J. (1977). *J. Chem. Soc. Chem.
  Commun.* pp. 824–825.

Chloro(dimethylphenylphosphine)gold(I)

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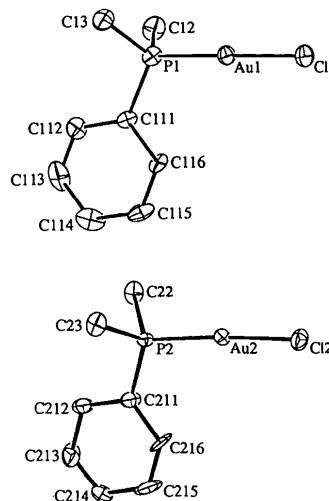Adelaide, SA 5001, Australia*

Fig. 1. Molecular structure of [(Me$_2$Ph)PAuCl] showing the crystallographic numbering scheme; diagram drawn at 30% probability levels (Johnson, 1976).

Abstract

Two molecules of [(Me$_2$Ph)PAuCl] comprise the asymmetric unit; these differ in the relative orientations of the phosphine-bound substituents. The Au—P bond distances are 2.214 (6) and 2.205 (5) Å for molecules (1) and (2), respectively; the Au—Cl distances are 2.276 (6) and 2.273 (6) Å and the P—Au—Cl angles are 177.2 (3) and 175.4 (2)°, respectively.

Comment

The geometries found for the independent Au atoms in [(Me$_2$Ph)PAuCl] are as found in related derivatives. Of interest is the systematic variation of the Au—P bond distances in complexes of general formula [R$_3$PAuCl]. Whereas the Au—Cl bond distances are equal within experimental error in the series of complexes R = *cyclo*-C$_6$H$_{11}$ (Muir, Muir, Pulgar, Jones & Sheldrick, 1985), R = *o*-MeC$_6$H$_4$ (Harker & Tiekink, 1990), R = Ph (Baenziger, Bennett & Soboroff, 1976), R = Et (Tiekink, 1989) and R$_3$ = Me$_2$Ph, the trend in the Au—P bond distances decreases in this order, *i.e.* Au—P 2.242 (4) for R = *cyclo*-C$_6$H$_{11}$, 2.243 (2) for R = *o*-MeC$_6$H$_4$, 2.235 (3) for R = Ph, 2.232 (9) and 2.231 (8) (two molecules) for R = Et, and 2.214 (6) and 2.205 (5) Å (two molecules) for R$_3$ = Me$_2$Ph; the relatively high experimental errors not withstanding. This trend follows that predicted from cone-angle considerations (Tolman, 1977).

The structure is molecular, there being no significant intermolecular contacts except for an Au(1)···Au(2) interaction of 3.262 (2) Å. The two independent molecules differ from each other in the relative orientations of the phosphine-bound substituents, as shown by the torsion angles Cl(*n*)—Au(*n*)—P(*n*)—C(*n*2),C(*n*3),C(*n*11) of −47, −165 and 72° for *n* = 1, and −178, 68 and −56° for *n* = 2, respectively.

Experimental

Crystal data

[AuCl(C$_8$H$_{11}$P)]
M_r = 370.6
Orthorhombic
$P2_12_12_1$
a = 12.639 (4) Å
b = 16.931 (6) Å
c = 9.458 (3) Å
V = 2024 (1) Å^3
Z = 8
D_x = 2.432 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25
  reflections
θ = 8.0–12.8°
μ = 148.550 cm^{-1}
T = 295 K
Block
0.27 × 0.27 × 0.14 mm
Colourless

Data collection

AFC-6R diffractometer
$\omega/2$-θ scans
Absorption correction:
  refined from ΔF (Walker
  & Stuart, 1983)
  T_{min} = 0.945, T_{max} =
  1.058
3015 measured reflections
2143 independent reflections
1608 observed reflections
  [$I > 3.0\sigma(I)$]

R_{int} = 4.58
θ_{max} = 25.3°
h = −1 → 15
k = 0 → 18
l = −11 → 0
3 standard reflections
  monitored every 400
  reflections
  intensity variation:
  −2.26%

Refinement

Refinement on F
Final R = 0.0350
wR = 0.0390
S = 2.380
1608 reflections
199 parameters
H atoms included in calculated positions
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max}$ = 0.0070
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)